

國立清華大學 命題紙

九十三年學年度 原子科學 系(所) 乙 組碩士班研究生招生考試

科目 分析化學 科號 3602 共 3 頁第 1 頁 \*請在試卷【答案卷】內作答

1. (10%) Spectroscopy is the use of the absorption, emission, or scattering of electromagnetic radiation by atoms or molecules (or atomic or molecular ions) to qualitatively or quantitatively study the atoms or molecules, or to study physical processes. Currently, several atomic spectrometries have been available for the determination of various metal ions in aqueous samples. Please finish following queries.
  - (a) Describe the basic differences atomic absorption and atomic emission spectroscopy.
  - (b) Why is the inductively coupled plasma (ICP) rarely used for atomic absorption measurements?
2. (10%) Combined chromatographic and various detection techniques and in particular liquid chromatography-mass spectrometry (LC-MS) have been contributing in a decisive way to the progress of life sciences in general. Please define following terms and illustrate their possible application in the characterization of bio-molecules.
  - (a) Size-exclusion chromatography
  - (b) Reverse phase chromatography
  - (c) Electrospray ionization mass spectrometry
  - (d) Spectrophotometry
3. (10%) Electroanalytical methods are techniques which encompass a group of quantitative and qualitative methods that are based upon the electrical properties of a solution of the analyte when it is made part of an electrochemical cell. Please state the fundamental working principle of following methods and their relation to charge of analytes, cell potential, and faradic current.
  - (a) Coulometric method
  - (b) Potentiometric method
  - (c) Voltammetric method
4. (10%) Mass Spectrometry is an analytical technique that is used to identify unknown compounds quantify known materials and elucidate the structural and physical properties of ions. In general a mass spectrometer consists of an ion source, a mass-selective analyzer, and an ion detector. Please finish following queries and state the fundamental working principle of the given examples.
  - (a) What types of ionisation are available? (please give two ionization methods)
  - (b) What types of mass analyser are available? (please give two mass analyzers)
5. (10%) There are several methods used to prepare aqueous buffer solutions, but the basic principle of all of them is the same: the solution must contain both the acid and the base of a conjugate pair, in reasonably similar and in reasonably high concentrations. Describe how you might prepare approximately 500.0 mL or at pH 4.5 buffer solution from 1.0 M acetic acid (HOAc) and sodium acetate (NaOAc). ( $K_a=1.75 \times 10^{-5}$ , M.W. of NaOAc = 82.034 g/mol)

國立清華大學 命題紙

九十二學年度 原子科學 系(所) 乙 組碩士班研究生招生考試

科目 分析化學 科號 3602 共 3 頁第 2 頁 \*請在試卷【答案卷】內作答

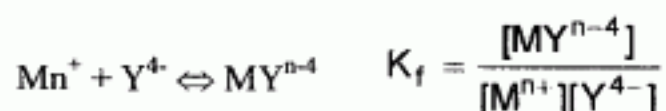
6. (10%) In 1857, Michael Faraday discovered that cyanide solutions could dissolve gold in cyanide solutions in the presence of oxygen. Sodium cyanide is a well-known compound that is often used as a poison and referred to in detective novels. If you are assigned to titrate 0.0500 M NaCN solution with 0.1000 M HCl. The reaction is



Please calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of acid.

( $K_a$  of HCN =  $6.2 \times 10^{-10}$ )

7. (10%) EDTA is the most commonly used chelating agents as it can form complexes with a wide range of metals. The ability of EDTA to complex is dependent on its form. The most desirable state is the  $\text{Y}^{4-}$  form. As the pH increases, more EDTA becomes  $\text{Y}^{4-}$ . The formation constant for metal-EDTA complexes is:

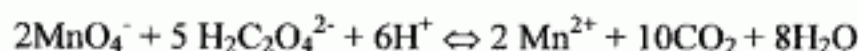


It is important to note the requirement for the charge state of EDTA. Leads to a conditional (effective) formation constant

$$K'_f = \alpha_4 K_f = \frac{[\text{MY}^{n-4}]}{[\text{M}^{n+}][\text{EDTA}]}$$

Based on the principle of EDTA complexation reaction, please calculate the equilibrium concentration of  $\text{Ni}^{2+}$  in a solution with a  $\text{NiY}^{2-}$  concentration of 0.0150 M at pH (a) 3.0 and (b) 8.0. (pH 3.0  $\alpha_4 = 2.5 \times 10^{-11}$ , pH 8.0  $\alpha_4 = 5.4 \times 10^{-3}$ ,  $K_{\text{NiY}} = 4.2 \times 10^{18}$ )

- (10%) 9. Chemical oxidation offers the several advantages over other treatment technologies. Many oxidants are currently being examined for remediation of trichloroethylene (TCE) dense non-aqueous phase liquid (DNAPL). Potassium permanganate was selected due to its relative stability and persistence, ease in handling, relatively low cost (~\$3.00/kg), and the ability to visually see results of the application. In order to examine the purity of potassium permanganate, oxalic acid is always used as standard for the titration of permanganate solution. A 50.00 mL of 0.05251 M  $\text{Na}_2\text{C}_2\text{O}_4$  was used to titrate 36.75 mL potassium permanganate solution. Please calculate the molarity of the  $\text{KMnO}_4$  solution.





國立清華大學 命題紙

九十二學年度 原子科學 系(所) 組碩士班研究生招生考試

科目 分析化學 科號 3602 共 3 頁第 3 頁 \*請在試卷【答案卷】內作答

9. (10%) The important concept for the environmental engineer is that many different biochemical and chemical reactions must interact to develop the oxidation-reduction potential of a solution. Electrons move, oxidation states change, and electromotive force can substitute for chemical potential in chemical oxidation and reduction. A half-cell is governed by the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \log \frac{Ox}{Red}$$

where E = electrochemical potential, volts

$E^{\circ}$  = standard potential, volts

R = universal gas constant

T = absolute temperature, ° K

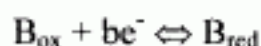
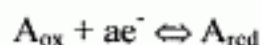
n = number of electrons transferred

F = Faraday's constant, 96,500 coulombs/equivalent

'ox' and 'red' are the activities of the oxidized and reduced ionic species.

At equilibrium, the electrode potentials for all half-reactions in an oxidation/reduction system are equal.

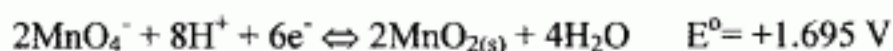
- (a) Please derive a general relationship for computing equilibrium constants from standard-potential data, where the two electrode reaction are



- (b) Please calculate the equilibrium constant for the reaction.



Where



- (10%) 10. Please differentiate between

- accuracy and precision
- systematic error and random error
- normal phase and reverse phase chromatography
- hard and soft ionization method
- single-beam and double-beam instruments for absorbance measurements